

# Thermal conductivity of water insoluble proteins: anharmonic coupling in a fractal structure

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## Introduction

Energy processes in proteins dictate biological and chemical functions. To offer insight into the mechanisms underlying thermal energy transport, we measure the thermal conductivity of solid, water insoluble, protein films via time domain thermoreflectance. We measure the thermal conductivities of solid myoglobin and bovine serum albumin (BSA) over a range of temperatures, 77-296 K. The measured thermal conductivities of the protein films display signatures of the presence of anharmonic coupling allowing us to evaluate current theories of anharmonicity in proteins presented in Ref. 1. Additionally, we apply a model of thermal conductivity in electrically insulating amorphous solids, presented in Ref. 2, which applies the anharmonic theory presented in Ref. 1. The model reproduces the measured thermal conductivities of the proteins. Furthermore, alike molecular dynamics results presented in Ref. 1 that described an energy-independent mean free path (MFP) of  $\sim 1$  nm, the model presented in Ref. 2 predicts that the majority of thermal conductivity accumulates with MFPs equal to or less than  $\sim 1.5$  nm.

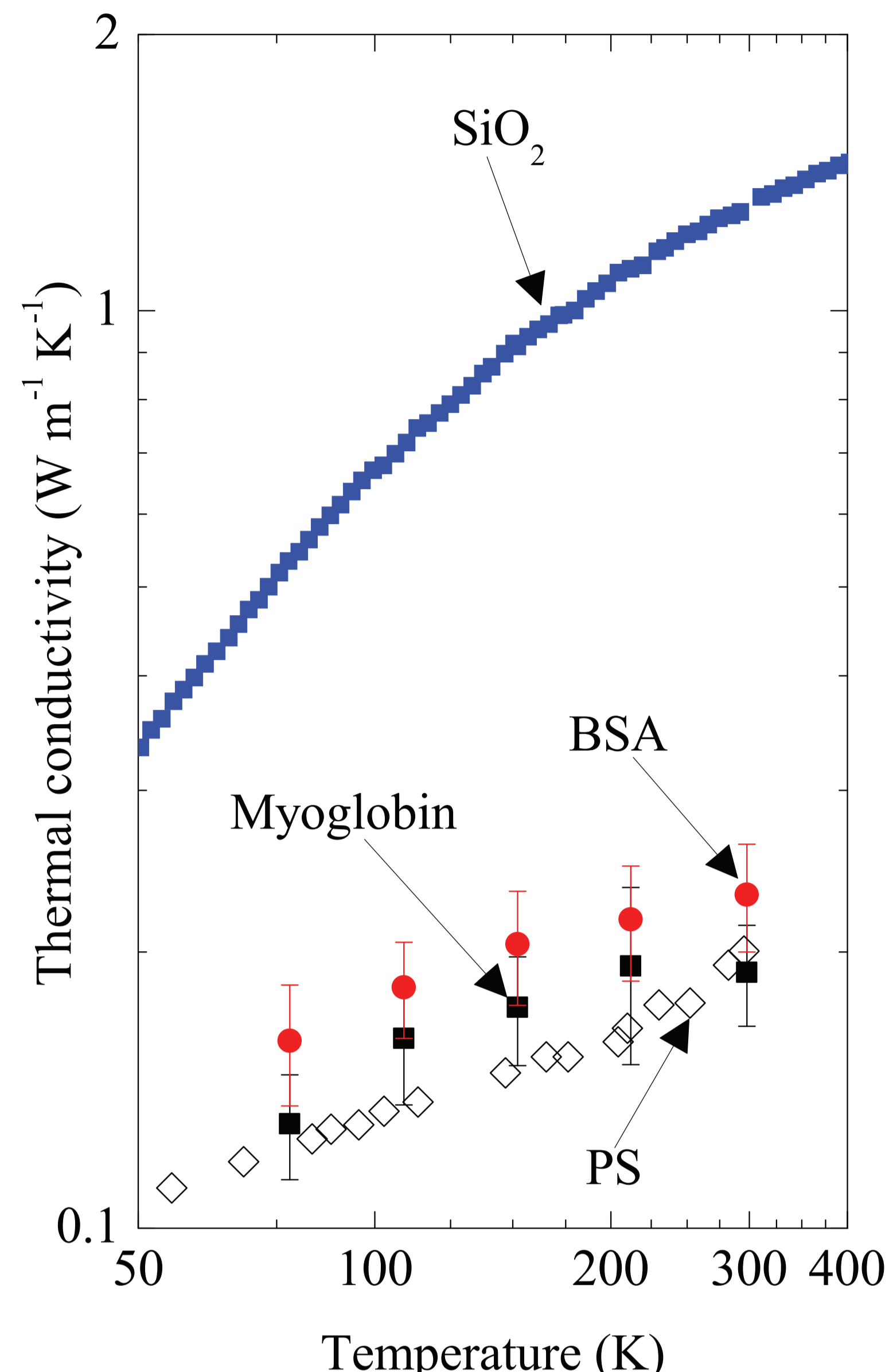


Fig. 1. Thermal conductivity of BSA and myoglobin (this work), SiO<sub>2</sub> (Ref. 3) and polystyrene (PS) (Ref. 4) are presented.

## Time domain thermoreflectance (TDTR)

TDTR is a non-contact, optical pump-probe technique used to measure thermal properties (Refs. 6 and 7).

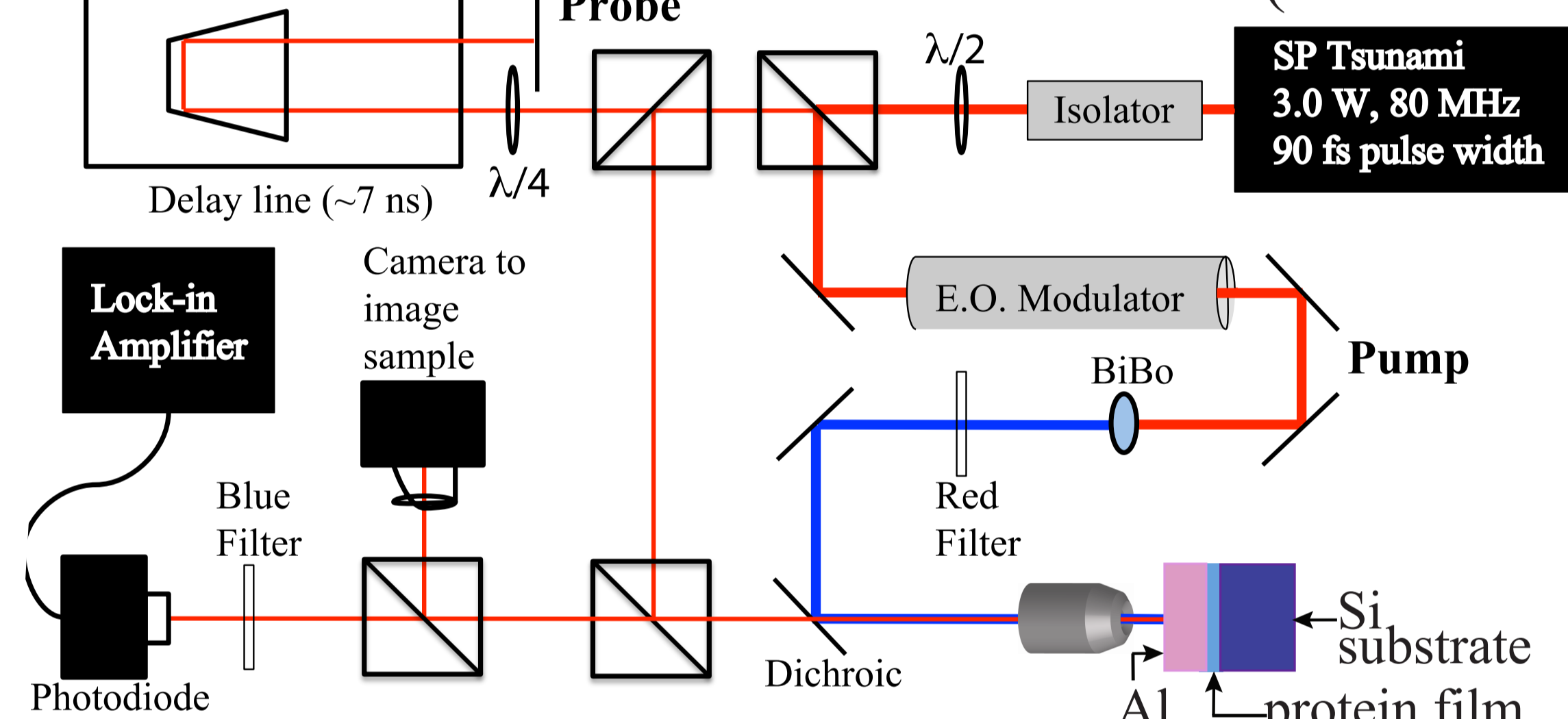


Fig. 4. A schematic of the femtosecond optical technique, TDTR, used to measure the thermal conductivity of solid proteins in this research.

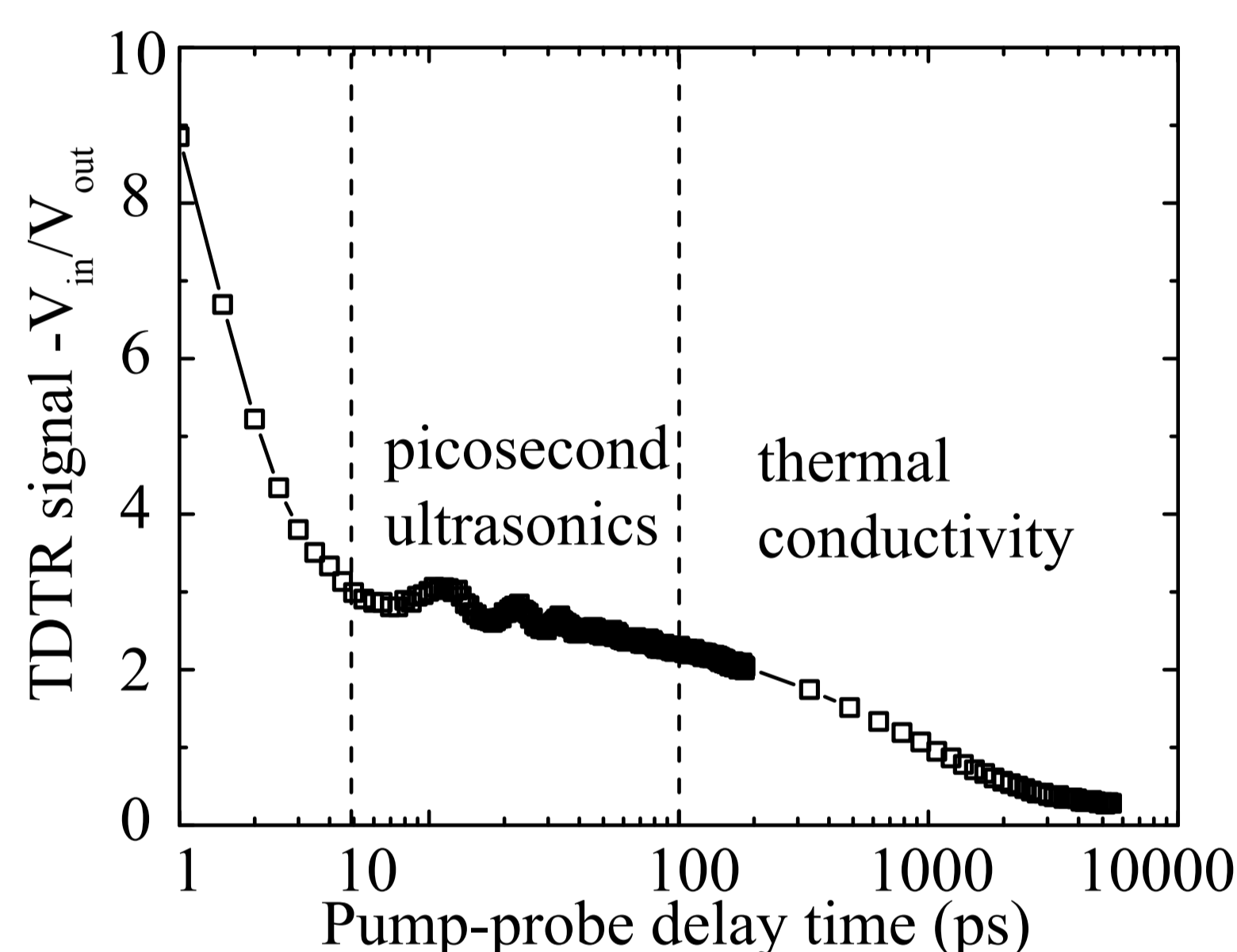


Fig. 5. Representative TDTR data set and a critical piece of information collected from each response regime.

## Thermal measurements and anharmonic theory

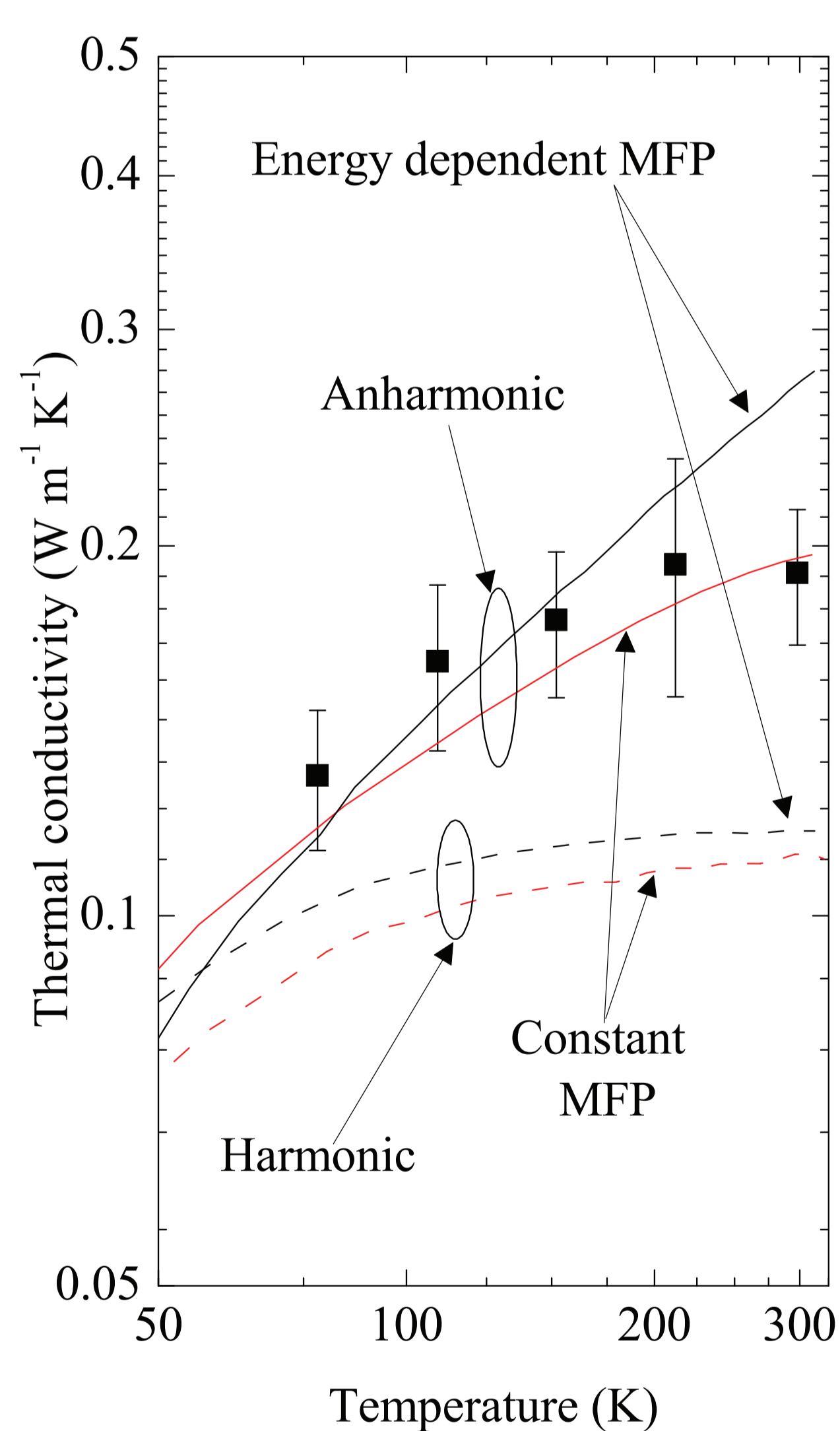


Fig. 6. Measured thermal conductivity of myoglobin (squares) compared to Yu and Leitner's harmonic and anharmonic models (Ref. 1).

- Fig. 6 compares the measured thermal conductivity of myoglobin (squares) to the models reported by Yu and Leitner (Ref. 1). The increase in thermal conductivity with temperature indicates that anharmonic vibrational coupling contributes to thermal resistance over this temperature region.

- Vibrational relaxation is theorized to occur harmonically if a mode does not lose quasi-momentum at its localization length,  $\xi$ . Conversely, if anharmonic relaxation occurs at  $\xi$  mode conversion will alter the vibrational quasi-momentum (Ref. 1).

- Using molecular dynamics methods, Yu and Leitner calculated the transition rate and  $\xi$  of the normal modes, under assumption of grey and specular distributions of MFPs, of myoglobin protein. The results of their simulations, shown in Fig. 6, indicate different temperature trends dependent on the spectral nature of the MFPs.

- Our data indicate that thermal transport in proteins is driven by vibrations interacting anharmonically with similar length scales, i.e., the grey approximation.

## References

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## Sample preparation and characterization

Films were prepared by adapting a method described in Ref. 5. Protein solutions were either drop-cast or spin-coated onto oxygen plasma silicon substrates to achieve thickness ranging from nanometers to microns. Spin-coating was performed at 500 rpm (30 sec) followed by 2000 rpm (30 sec) yielding  $\sim 30$  nm thick films.

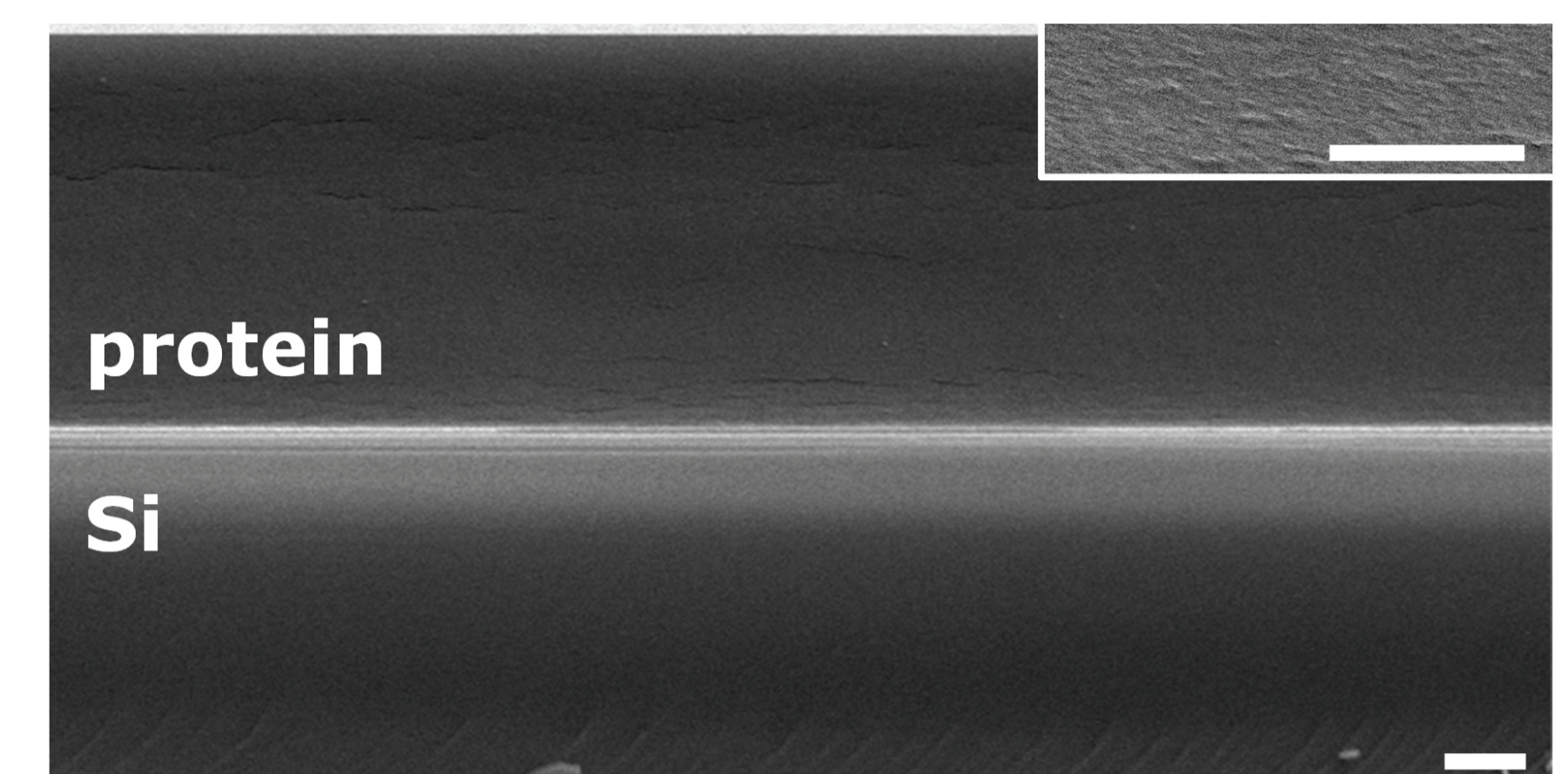


Fig. 2. Scanning electron microscopy cross-section image of a BSA protein film drop-cast onto a silicon substrate. Inset shows higher magnification of the solid protein film. Scale bars, 1 micron.

Circular dichroism spectroscopy (CD) characterized the physical structure of the protein. The CD signal indicated the films are not denatured. Ellipsometry determined thicknesses.

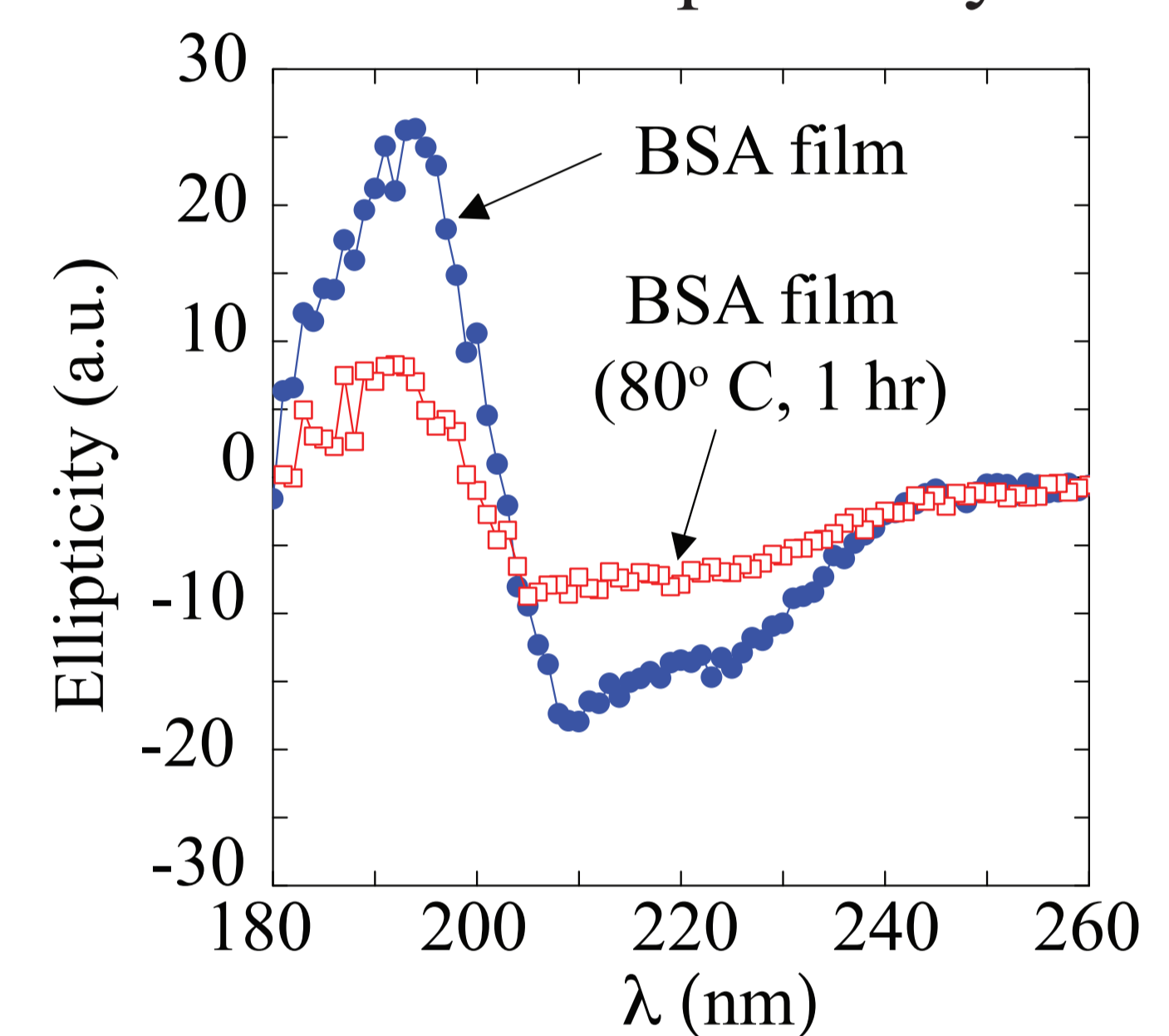


Fig. 3. CD spectra of the protein thin film of BSA before (filled) and after (unfilled) heat treatment. The characteristic double minimum for the unheated films confirms the intact helix comprising the secondary structure.

## Further discussion

Vibrational modes in proteins, alike the modes in other insulating solids, are theorized to experience unique scattering events dependent on their length and energy scales. We theorize that frequency-dependent boundary scattering inhibits conduction of non-propagating, diffusive vibrations. Anharmonic processes drive the thermal resistance due to vibrations with high quasi-momentum (Ref. 1).

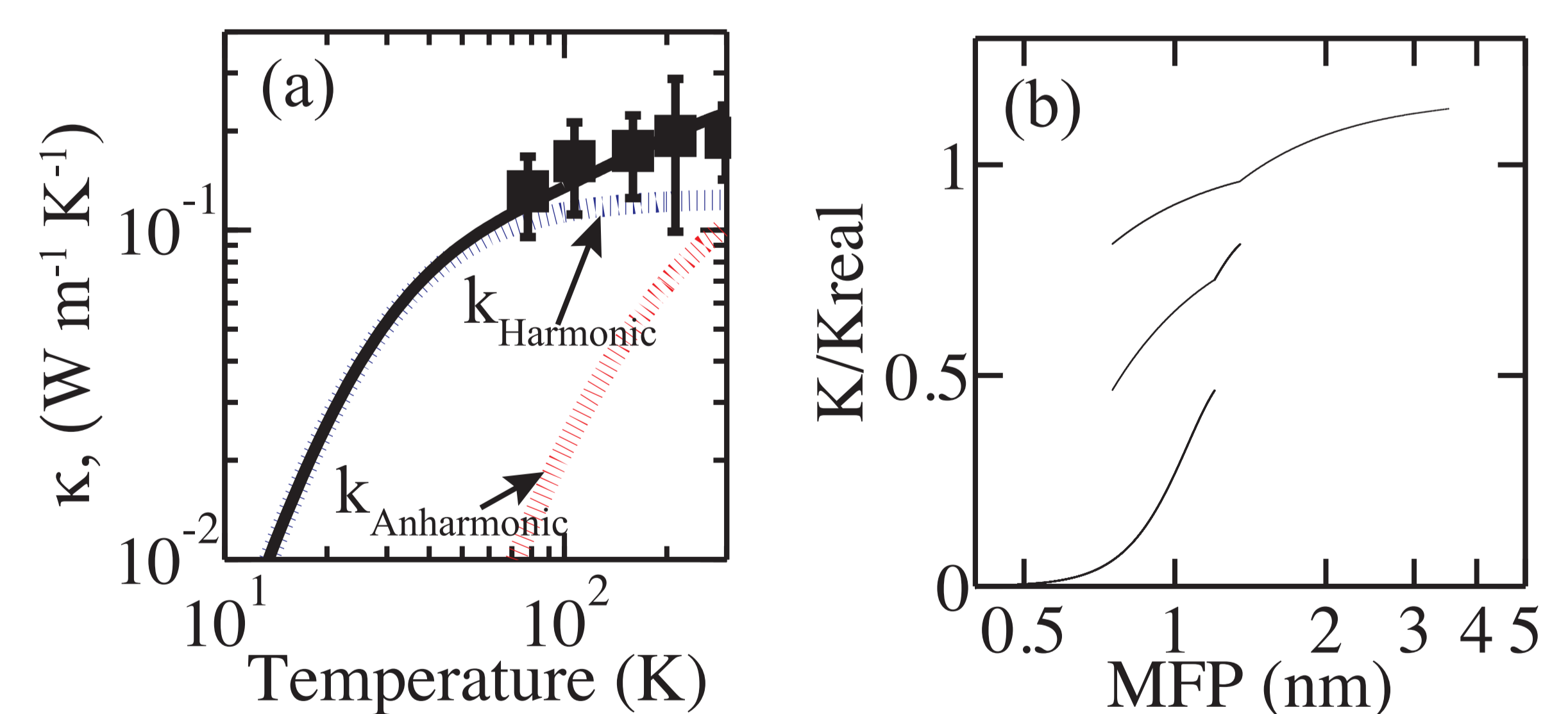


Fig. 7. (a) Measured thermal conductivity of myoglobin (squares) presented alongside the \*theoretical  $\kappa_{\text{protein}}$  (solid line) (Ref. 2) and, (b) the \*theoretical thermal conductivity accumulation as a function of vibrational MFP.

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## Conclusions

In summary, we measured the thermal conductivity of solid, water insoluble, protein films of BSA and myoglobin from 77 K to room temperature. The thermal conductivity of the proteins increases with increasing temperature, indicating that anharmonic vibrational coupling contributes to thermal conductivity in proteins. This trend is reproduced theoretically upon applying the theory of vibrations in dielectric solids presented in Ref. 2 to proteins. Relaxation mechanisms, harmonic and anharmonic, resulting in thermal conductivity in protein have been further investigated through calculation of a theoretical thermal conductivity accumulation, Fig. 7(b), as a function of vibrational mean free path. Neglecting possible contribution from continuum-type vibrations, the model predicts the majority of thermal conductivity to be due to vibrational states scattering within  $\sim 1.5$  nm. Further understanding of energy transport in protein will continue as the normal modes of the system and their origins are understood and characterized.

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